

Microprobe Two-step Laser Mass Spectrometry Using Extreme Ultraviolet Photoionization: Analysis of Astromaterials

Simon J. Clemett, Johnson Space Center

Scott Messenger, Johnson Space Center

The human race has only just begun to take the first tentative steps toward interplanetary travel. Nevertheless, it is already possible to directly study, in the laboratory, fragments of the asteroid belt, the stuff from which comets are made, rocks from the surface of Mars, the wind from the sun, and—perhaps most remarkable of all—the dust that fills the void between the stars. These samples are brought by meteorites and interplanetary dust particles accreted by the Earth, and by the recent sample return missions—Genesis, Stardust, and Hayabusa. The laboratory study of these materials gives us a means of exploring the origin and evolution of the galaxy and the solar system.

Johnson Space Center's research in the Astromaterials Research and Exploration Science (ARES) Directorate focuses on the analysis of organic species in astromaterials. Organic matter is pervasive throughout the galaxy and solar system. Hundreds of organic molecules have been identified in interstellar clouds, primitive meteorites, and comets, and are formed by complex chemical processes in diverse environments.

Carbon is unique in its capacity to form hybridized molecular bonding orbitals and, thus, self-catenate. As a consequence, organic molecules take a staggering variety of forms; the number of organic compounds exceed those

from all other elements combined. By virtue of this diverse chemistry, organic matter preserves a detailed record of its physical and chemical formation and subsequent alteration processes. By deciphering this record, light can be shed on interstellar chemical processes and conditions in the early solar system. However, these analyses present a number of significant challenges:

- Certain organic species may only be present in trace concentrations, parts per million or less.
- Organic matter may consist of complex mixtures containing hundreds or thousands of species.
- Samples are limited and/or extremely heterogeneous.
- Samples are unique and hence precious.

The ARES team has designed and constructed a unique microprobe two-step laser mass spectrometer (μ -L²MS) to measure organic compounds with great sensitivity, selectivity, and spatial resolution (figure 1). A key feature of this instrument is that molecules are vaporized and ionized in two separate steps with independent laser sources. In the first step, a pulsed infrared laser is focused on the sample to cause rapid, localized heating. In the second step, a pulsed ultraviolet (UV) laser ionizes some of the molecules desorbed by the first laser. Which molecules

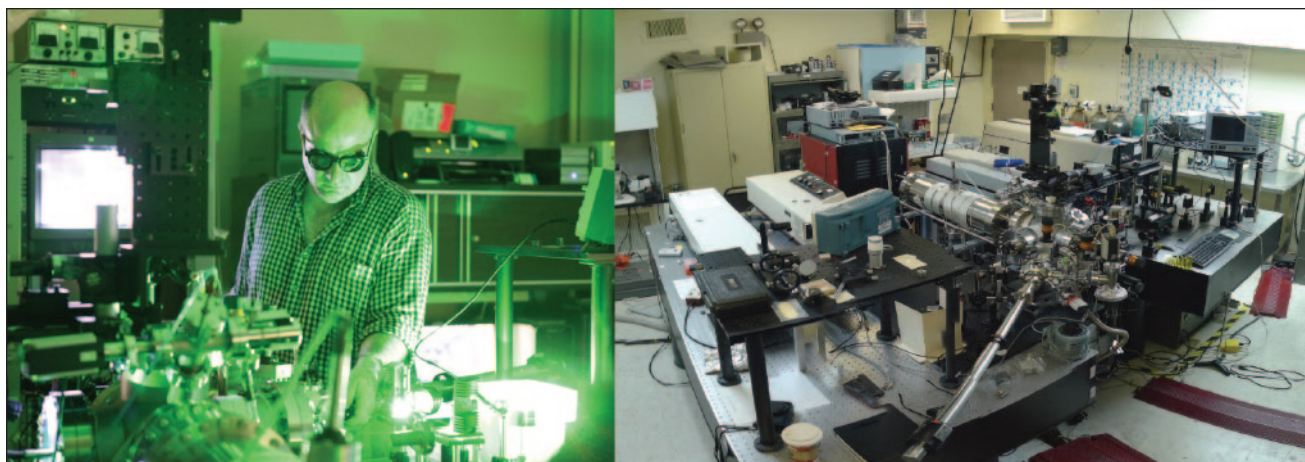


Fig. 1. Astromaterials Research and Exploration Science microprobe two-step laser mass spectrometer (μ -L²MS) laboratory.

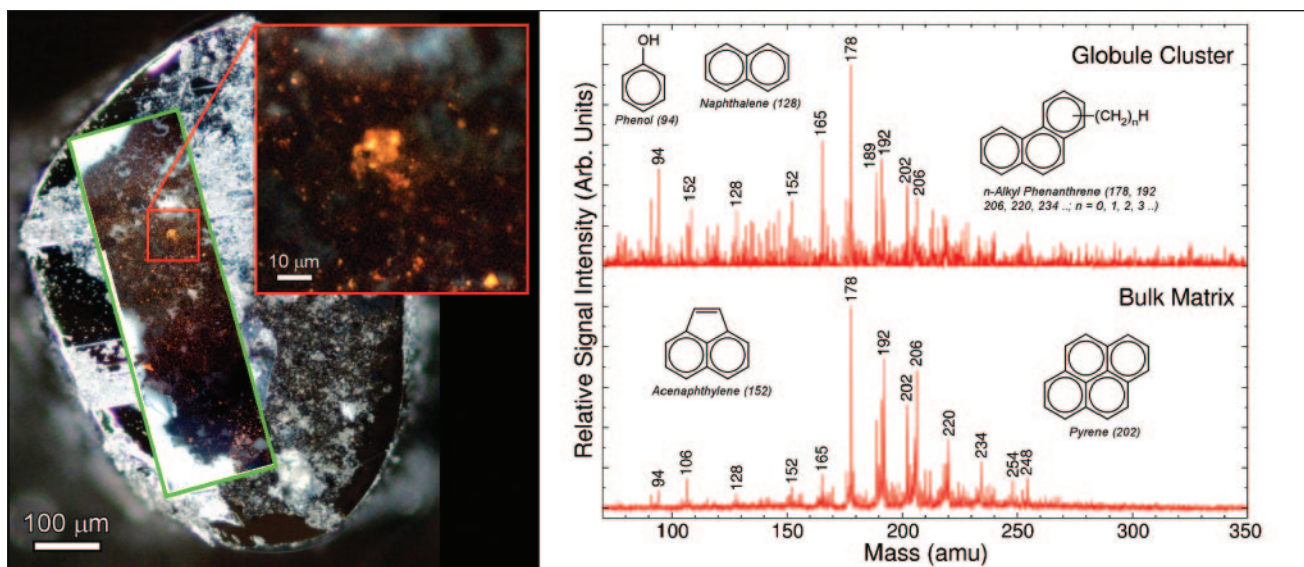


Fig. 2. Microprobe two-step laser mass spectrometer (μ -L²MS) of a nanoglobules cluster in the Bells (CM2) chondrite. The left panel shows the optical image of the microtomed surface on which is overlaid a native fluorescence image in which a globule cluster is identified and shown magnified. In the right panel, the μ -L²MS spectra obtained on the globule cluster is compared to that of the averaged surface. While both globules and bulk organic composition share a similar distribution of multiply alkylated 3-4 ring polycyclic aromatic hydrocarbons, there is a distinct difference in their distributions of lower molecular weight (< 178 atomic mass unit) species.

are ionized depends on their spectroscopic properties and the wavelength of the UV laser light. The resulting ions are then mass analyzed in a reflectron time-of-flight apparatus. The design of the instrument makes it possible to measure organic molecules intact, avoiding fragmentation in both the vaporization and ionization steps. Consequently, the μ -L²MS instrument can be used to analyze mixtures of molecules in complex materials without extraction, purification, or other complex sample preparation. Moreover, it is capable of micrometer spatial resolution so that the organic measurements can be correlated to mineralogical features of the sample.

The ARES team has analyzed organic matter in a wide range of astromaterials with the μ -L²MS instrument, including carbonaceous and ordinary chondrite meteorites, Martian meteorites, Antarctic micrometeorites, interplanetary dust particles, interstellar graphite grains, interstellar ice analogs, and Stardust cometary dust

particles. For example, figure 2 illustrates the analysis of a cluster of organic nanoglobules embedded within the matrix of the Bells (CM2) chondrite. In work published by lead author Keiko Nakamura-Messenger, also of ARES, the work showed that these organic globules are older than the Earth and may have originated in a cold interstellar cloud.

A limitation of the μ -L²MS instrument has been that the range of organic compounds that could be studied has been restricted to species containing aromatic and/or conjugated functionalities. This is a consequence of the 1+1 Resonance Enhanced Multi-Photon Ionization (REMPI) process that was used. In this scheme, photoionization occurs through the successive absorption of two UV photons; absorption of the first photon causes excitation into a rovibrational manifold of the first electronic excited state, resonant adsorption of a second photon then leads to ionization. Using a 266 nanometer (nm) (~4.3 electron volt/photon [eV/photon]) UV laser source, the only

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continued

accessible intermediate excited electronic state in organic molecules corresponds to a $\pi\text{-}\pi^*$ transition, hence the restriction to aromatic and/or conjugated species.

To expand the range of compounds that can be detected, the ARES team has developed and is currently incorporating a coherent vacuum ultraviolet, single-photon ionization source that will complement the team's existing $\mu\text{-L}^2\text{MS}$ capabilities (figure 3). The generation of coherent vacuum ultraviolet radiation is achieved by the nonlinear frequency tripling of the 3rd harmonic (λ 355 nm) of a mode-locked Q-switched picosecond neodymium: yttrium-aluminum-garnet (Nd:YAG) laser in a xenon-argon gas cell to produce 118.2 nm (~ 10.5 eV/photon) radiation. Efficient phase matching of 118.2 and 355 nm photons is possible due to the negative dispersion of xenon in the region 117.2 to 119.2 nm due to the 5p-5d electronic transition, allowing conversion efficiencies of approximately 0.01%. Since the first ionization potential for nearly all organic molecules lie in the range of 5 to 10 eV, effectively all organic species can be photoionized by such vacuum ultraviolet photons. Furthermore, this provides both an efficient and a "soft" ionization process comparable to that currently achievable with the team's (1+1) REMPI source. The team hopes that its new $\mu\text{-L}^2\text{MS}$ and its future successors will become another powerful instrument in the arsenal that astrochemists have for exploring and understanding the universe.

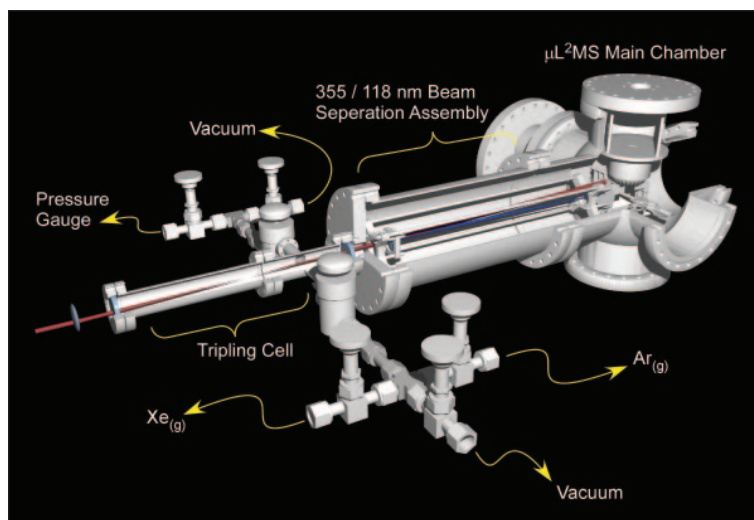


Fig. 3. Ray-traced illustration of 3rd harmonic generator for production of 118.2 nm coherent radiation. Frequency tripling occurs within a low pressure xenon-argon gas cell at the beam waist of a focused 355 nm laser pulse. Separation of the 3rd harmonic from the fundamental is done in vacuo within the $\mu\text{-L}^2\text{MS}$ chamber using an off-axis plano-convex magnesium fluoride focusing lens.